A THERMODYNAMIC STUDY OF THE LIQUID Pb·Bi ALLOYS AT 823°K

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By
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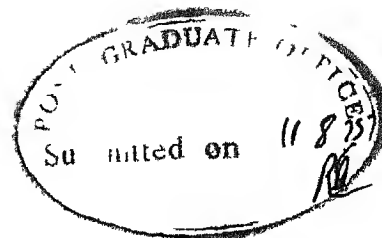INDIAN INSTITUTE OF TECHNOLOGY KANPUR
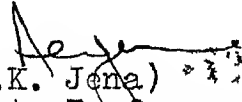AUGUST, 1975

CERTIFICATE

This is to certify that the work 'A THERMODY-

NAMIC STUDY OF THE LIQUID Pb-Bi ALLOYS AT 823°K' has been

carried out by Kumari Vijayakumari C. Das under my

supervision and that it has not been submitted elsewhere

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CHAPTER - I

INTRODUCTION

In recent years molten metal systems have been examined in the light of various kinds of experimentally measured quantities. All these methods contribute in varying degrees to the structural and thermodynamic properties. The thermodynamic properties of liquid alloys are much useful in case of extraction, refining, alloy making, theory of alloys. Especially low melting alloys like Pb-Bi are needed in the reactors for heat transfer purposes and other nuclear engineering applications.

In this contest the low melting Pb-Bi alloys are of importance. The melting point of lead in $327^{O}C$ and ___ that of bismuth is $271^{O}C$. These two metals form a eutectic system with a eutectic temperature of only $125^{O}C$. The lead is more electropositive than bismuth in the electro-chemical series. In this investigation the thermodynamic properties of this system has been measured at $823^{O}K$ by the e.m.f. technique and the structural characteristics of these alloys have been discussed.

CHAPTER - II

REVIEW OF LITERATURE

2.1 Various Methods[1,2]

In one of the methods the vapour pressure of one
of the components of the alloy is measured as a function of
composition. Many experimental methods have been recently
developed for this purpose. It is possible to calculate
various thermodynamic properties from this data Though
the results of the evaporation studies have yielded much
useful thermodynamic information it is not sufficiently
reproducible to provide much information concerning the
structure and nature of the bonding in the surfaces of
solid materials.

The calorimetric technique measures the changes
in the enthalpy of heat content of substance, associated
with changes in temperature, changes of states such as melting
and boiling, changes of chemical combination such as
reactions and alloying, dissolution or changes of physical
structure, annealing, recovery and grain growth etc. But
it is not possible to measure heats of reaction at low
temperatures directly. The energy change of interest may
have to be obtained as the small difference between two
large quantities with the consequent need for high precision

in the measurement. These methods measure the total energy difference between two states and kinetic studies are therefore tedious.

The well-known three electrochemical techniques are the ones which use the aqueous, molten and solid electrolytes for the determination of the thermodynamic quantities. Because of the evaporation of electrolyte at working temperatures the scope of the former one is limited. For high temperatures solid electrolytes are most convenient. But many systems can not be investigated with solid electrolyte particularly at low temperatures as the electrolyte must have a minimum conductivity of 10^{-6} ohm^{-1} cm^{-1} which is only achieved at elevated temperatures. Moreover its use is limited because of the appearance of the electronic conductivity under highly reducing conditions The molten electrolyte technique has got the advantage that the required conducting ion may be brought into the neutral fused halides, oxides, acetates melts by dissolving small amounts of the salt or compound for the conducting ion in the suitable melt. By this technique the thermodynamic properties of binary, ternary, quarternary systems etc. intermetallic compounds, carbides, sulphides etc. can be studied.

2.2 The E.M.F. Technique

Theory: It is possible to obtain the changes in free
energy of a reaction by measuring the e.m.f. of a suitable
galvanic cell where the reaction is made to occur electro-
chemically[3]. Thus in the following chemical cell,

$$M/MX/X$$
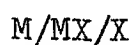
where MX is the electrolyte (an ionic conductor) and the
electrodes M and X gives an e.m.f. This e.m.f. is related
to the standard free energy of formation of MX by the
expression

$$\triangle G^o_{MX} = - nEF$$

where all the components are in their standard states and
n is the number of electrons transferred during the reaction,
F is the Faraday constant and E is the e.m.f. . If one
measures the e.m.f. as a function of temperature their
enthalpy and entropy changes can also be estimated.

One of the most important information available
by this technique is the activity of a component in a
binary or a multicomponent system. The reversible cell
of the following type can be constructed for this purpose

Pure metal (A)	Electrolyte containing ions of metal (A)	Solution of metals (A) and (B)

If one gm-atom of metal is transferred from pure metal to an alloy the amount of work done is,

$$RT \ln a_A = - nEF$$

And a_A can be found out. To obtain reliable thermodynamic data one must however arrange to have well defined experimental conditions. So the following points should be kept in mind.

    1. All exchange reactions between the alloy and the electrolyte must be absent.

    2. Atmosphere surrounding the cell must not take part in the reaction.

    3. Diffusion in the alloy must be fast to maintain a homogeneous alloy electrode.

    4. Electrolyte must be purely ionic.

    5. The electrodes and the electrolytes used must be pure.

    6. Reversibility of the cell must be established beyond doubt.

    Actually there is no single criterion which establishes the reversibility of an electrolytic cell But if the following points are satisfied by any cell we can assume the cell to be reversible.

ı)   The e.m.f. values obtained on heating and cooling coincides within the limits of experimental errors.

ıı)   There should be no attack apart from a slight etch on the electrodes and there should not be any detectable change in their surface compositions.

ııı)   The potentials measured by a null method were in themselves **should** be reversible.

ıv)   The side reaction should not be present. If any such reaction is present corrected values should be taken[4].

Electrolyte.   A large number of investigations have been carried out using the fused salt electrolyte[5-33,40-44]. An eutectic mixture of AgCl + KCl was used by Ölander[5]. Pure fused $Ag_2(NO_3)_2$ and molten solution of AgCl was used by Watcher[6]. An eutectic mixture of KCl and LiCl and some amount of baser chlorides were used by a number of workers[7,12-14,16,19,20-23,26-30,32,33]. Molten equimolar mixture of KCl and NaCl with small amount of baser chlorides were used by Egan[21], Pratt[8] and Seigle[15]. Molten equimolar solutions of $AgCl_{\not{y}}$ and NaCl were used by Hillert et al[10]. The mixture of KCl, NaCl, $AlCl_3$ were used by Wilder[11]. Mixture of LiCl and RbCl, sodium and potassium acetates were used by Ölander[13]. Eutectic mixture of LiBr and RbBr was used by Trunbore et al[25].

<u>Purification of Electrolyte</u>   Metallic sodium was added
to the electrolyte   by Kleppa[12] to reduce oxidation
of metal due to the traces of H_2O present. Olander[13]
added $CdCl_2$ and Cadmium acetate to the electrolyte.
Oriani[11] added RbCl. Seigle[15] had added .2 mole pct.
of $FeCl_2$ and .5 mole pct. of NH_4Cl. Fused KOH was added to
neutralise the Hydrogen ions which might have formed from
hydrolysis of moisture in the salt by Chipman and Elliott[19]
and Taylor[20]. NH_4Cl was added by Melgren[32] for
preventing hydrolysis For the same reason Trunbore et al[25]
added NH_4Br.

Wagner[34] heated the mixture of LiCl, KCl and
$CdCl_2$ with NH_4Cl at $350^{o}C$ until all NH_4Cl wds vapourised.
He also melted LiCl, KCl, $SnCl_2$ under stream of purified HCl
and subsequently in purified N_2. Rosenthal et al[31]
dehydrated the electrolyte under vacuum at $150^{o}C$ before
placing it in the shell and the final dehydration was
affected by the application of moderate heat at 10^{-3} mm of
Hg. Elliott and Chipman[19] melted KCl, LiCl at $400^{o}C$,
added fused KOH and small amount of Cadmium pellets and
then the temperature was raised to $500^{o}C$. After one hour
the temperature was lowered to $400^{o}C$ The electrolyte was
finally filtered through pyrex glass wool. Hillert et al[10]
purified the electrolyte by electrolysis at $350^{o}C$ for
24-36 hours with 2 V between graphite electrodes under an

atmosphere of dried argon. Laitinen et al[35] evacuated
the mixture of LiCl, KCl at .15 to .2 mm Hg for 6 hours.
Then ground it to a fine powder by ball mill. Evacuated
this for 3 days and raised the temperature to $300^{\circ}C$ in
8 hours The temperature was again raised to $500^{\circ}C$, HCl
was passed, the cell was evacuated and it was filled with
argon. The cell was again evacuated and filled with argon
Gardner et al[36] ground the fresh chlorides to ASTM 30 mesh,
heated to $100^{\circ}C$ under vacuum and then raised the temperature
to $500^{\circ}C$. These chlorides were mixed in a dry box and
transferred to the cell. Salomons et al[37] carried out
similar process as Gardner et al[36] and in addition to
it they treated the mixture with HCl and evacuated for
a long time. Oriani[7] prepared equimolar mixture of KCl,
LiCl and some amount of AgCl and CuCl in separate
container by holding at $500^{\circ}C$ in contact with pure Ag or Cu
wire for atleast 3 days under vacuum of about 1 μ Hg.
Meanwhile the cell itself was prepared by holding it under
the same vacuum at a temperature above the melting point
of the alloy. The electrolyte was forced in to the cell
by pure helium. Pratt[8] dehydrated the equimolar mixture
of KCl, NaCl by prolonged heating under vacuum. The
mixture of alkali halides with some NH_4Cl was loaded in
to a recrystallized alumina crucible and placed in a
continuously evacuated and heated silica chamber. The

temperature was progressively raised from $200^{\circ}C$ to $660^{\circ}C$ in 7 days. .1 mole pct. of AgCl which had been similarly dehydrated at $200^{\circ}C$ was added to the molten salt. Kleppa[12] melted LiCl and KCl in a cell and degassed by heating for sometime at $600-650^{\circ}C$. Metallic sodium was treated with it in molten state. Oriani[14] took KCl and LiCl in an auxiliary container and held at $400^{\circ}C$ in contact with pure Cu wire under constant evacuation for 4 days Some amount of RbCl was added to attain lower temperatures without freezing of the electrolyte. Melgren[32] dehydrated KCl and LiCl separately at $230-250^{\circ}C$ in 24 hours. NH_4Cl was added which decomposed to HCl and NH_3. The salt mixture was melted in an argon atmosphere and heated slowly to $600^{\circ}C$.

Electrodes: The solid electrodes were used by a number of people[5-10,14,15,25,28,32]. The electrodes in the liquid form were used by a number of workers[11-13,16-19, 21-24,26,29-31,33].

Olander[5] prepared alloys from .999 Au and .99975 Ag. Electrodes used by Oriani[7,14] were 99.99 pct. pure. Pratt[8] used 99.99 pct. pure Ag and 99.95 pct. Pd. Wilder[11] used 99.999 pct components. Kleppa[12] used Bi containing .03 pct. Au and Tl containing .007 pct. Au. Olander[13] used components pure up to .9999. Kleppa[18]

used Sn containing less than .04 pct. Pb, less than .01 pct.
Fe, less than .004 pct. Cu and Sb, less than .002 pct. Bi.
Au used was 99.9 pct. pure. Chipman and Elliott[19] used
Pb in amounts equal to .001 of atom fraction of Sb in case
of Cd-Sb alloys. Strickler and Seltz[22] used metals
purified electrolytically, the Pb being plated from Bott's[38]
bath and Bi by a method described by Swift[39]. Seltz and
Dunkerley[23] used chemically pure Sn containing less than
.01 pct. of impurities. Trunbore et al[25] used samples
free of metallic impurities within .02 to .05 pct. Seltz
et al[26] used commercially pure Cd containing less than
.005 pct. impurities. Rosenthal[31] used Pb 99.9995 pct.
pure and Zn 99.999 pct.

E.M.F. Measurements   The lead wires used for measuring
the e.m.f. was Ag welded with Cu wires[5,8]. A number of
investigators used W lead wires[7,12,16-20,23,24,32,33]
Hillert et al[10] used Al protected by quartz tubes.
Wilder[11] and Egan[21] used Ta lead wires. Oriani[28]
used Pt suspension wires which were Ag soldered with W wires.
Hildebrand and Sharma[30] soldered W wires with heavy Au
wires

    Reproducibility of measurements have been
reported to be ± .01 mV[17,10], ±0.02 mV[26], ± 0.05 mV[19,30],
± .1 mV[5,6,9,17,33], ± 0.2 mV[17], ± 0.3 mV[24] **and**
± .5 mV[12].

Temperature Measurements For temperature measurements chromel-alumel[5,6,11,17,19,21,30], iron constantan[22] and Pt-Pt, Rh (10 pct.)[7,31] thermocouple have been used. The temperature ranges used for the e.m.f. measurements are shown in Table 2.1.

2.3 The Pb-Bi System

The Pb-Bi alloys can be used to form a cell of the type given below.

$$\text{Pb} \mid \text{KCl} + \text{LiCl} + \text{PbCl}_2 \mid \text{Pb-Bi}$$
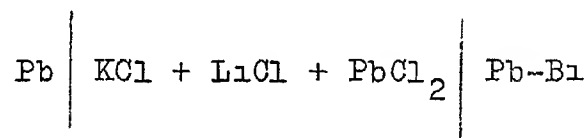
The difference in the standard free energy of formation of chlorides of the components in the binary system investigated by the e.m.f. techniques are shown in Table 2.1.

At 500°C , G° of formation of $PbCl_2$ from its components[3] is -58 Kcal/mole and for $BiCl_3$, -38 Kcal/mole. Since the difference of $\triangle G^{\circ}$ is 20 Kcal/mole which is quite appreciable amount, this cell is feasible (Table 2.1)

Table 2.1

Temperature Ranges and $\perp$ (ΔG^O)$^{\oplus}$ for Chlorides

System	Components whose activity is measured	Range of temperature $^O K$	$\perp (\Delta G^O)$Kcal for chlorides	Reference
Ag-Pd	X_{Pd} = .1-.95	1000		8
Ag-Sb	X_{Sb} = .322-.622	478-648	0.5	41
Ag-Sb	X_{Sb} = .024-.316	673-773	0.5	42
Ag-Sn	X_{Sn} = .3-.9	900	20.0	9
Ag-Sn	X_{Sn} = .86-.994	608-686	20.0	11
Ag-Zn	X_{Zn} = .28-.82	773-873	35.0	43
Al-Zn	X_{Zn} = .05-.9	560-820	49.5	10
Au-Cd	X_{Cd} = .56-.99	520-580	74.0	13
Au-Cd	X_{Cd} = .16-.76	640-870	74.0	13
Au-Cu	X_{Cu} = .42-.78	620-760	47.0	14
Au-Cu	X_{Cu} = .15-.85	120-131	47.0	7
Au-Tl	X_{Tl} = .8-.9	723-1023		12
Au-Sn	X_{Sn} = .22-.9	773-873	35.0	18
Bi-Cd	X_{Cd} = .1-.95	673-873	30.0	19
Bi-Cd	X_{Cd} = .25-.85	683-748	30.0	32
Bi-Cd	X_{Cd} = .164-.857	695-1123	30.0	20
Bi-Mg	X_{Mg} = .1-.85	763-1123	89.0	21
Bi-Pb	X_{Pb} = .005-.95	392-743	23.0	22
Bi-Sn	X_{Sn} = .10-.89	608	20.5	23

Table 2.1 continued.

Bi-Zn	$X_{Zn} = .064-.974$	692-923	35.50	24
Cd-Pb	$X_{Pb} = .063-.89$	648-873	7.0	19
Cd-Pb	$X_{Pb} = .214-.871$	700-845	7.0	20
Cd-Sb	$X_{Sb} = .519-.858$	648-823	30.0	19
Cd-Sb	$X_{Sb} = .104-.6556$	643-788	30.0	26
Cd-Sn	$X_{Sn} = .05-.9$	648-893	9.5	19
Cd-Sn	$X_{Sn} = .15-.75$	773	9.5	32
Cd-Sn	$X_{Sn} = .15-.9$	703-858	9.5	20
Cd-Sn	$X_{Sn} = .18-.92$	633-713	9.5	27
Co-Pt	$X_{Pt} = .27-.68$	970-1181		28
Pb-Sb	$X_{Sb} = .1-.31$	700	23.0	33
Pb-Sb	$X_{Sb} = .13-.84$	643-903	23 0	29
Pb-Sn	$X_{Sn} = .33-.67$	773	0.5	33
Pb-Sn	$X_{Sn} = .91-.99$	683-823	0.5	44
Pb-Zn	$X_{Zn} = .04-.99$	692-923	12.5	24
Pb-Zn	$X_{Zn} = .04- 99$	873	12.5	31
Sb-Sn	$X_{Sn} = .1-.9$	905	20.5	9
Sb-Sn	$X_{Sn} = .86-.92$	685	20.5	17
Sb-Zn	$X_{Zn} = .15-.92$	753-893	25.0	29
Sn-Zn	$X_{Zn} = .14-.85$	704-843	15.0	20

⊕ Values are taken from reference (3).

CHAPTER - III

EQUIPMENT AND PROCEDURE

3.1 Furnace and Temperature Control

A non-inductive nichrome wound tube furnace of 40 ohms resistance was used. The furnace was 60 cms long and 57 mm I.D. The winding was in the middle 35 cms of the furnace tube. 20 cms of the furnace tube was closed at the bottom by a refractory brick. A bottom closed chromium plated nickel tube of 0.5 mm thickness and 20 cms length was placed inside the furnace and earthed to avoid pickup of any induced e.m.f. as well as to homogenise the furnace temperature. A Leeds and Northrup temperature controller was used A 20 ohms resistance was connected to the relay of the controller such that in the off position about 60 pct. of the current was allowed to pass through the furnace A 36 gauge chromel-alumel thermocouple was placed between the nickel jacket and the furnace tube and connected to the controller. The cold junction of the thermocouple was placed inside ice-water bath. In this way the temperature of the furnace was controlled to $\pm$ $2^{\circ}C$ for a period of 24 hours

3.2 Design and Fabrication of Cell

The cell was made in a quartz crucible of 45 mm
O.D. and 10 cms height. The crucible had a optically flat
bottom and two small holes at the top This crucible
rested on quartz beads placed at the bottom of another
quartz tube of 50 mm O.D. and 50 cms long The quartz tube
was used so as to be able to evacuate the system at high
temperatures The outside quartz tube had a B-60 high
vacuum ground quartz joint attached to the open end. This
tube was closed by a B-60 high vacuum ground pyrex joint.
The pyrex joint was connected to a closed end 50 mm O.D.
pyrex tube. This tube had two side tubes at 180° apart
for inlet and outlet of argon gas. The outlet side tube
carried a two-way stop cock and extended 20 cms inside the
cell as shown in figure 2.1. So as to prevent short
circuiting of gas flow. The inlet side was connected to a
three way stop cock through a ground glass joint to have
connections to the vacuum pump and the gas line Four tubes
of 12 mm diameter were connected on the top of the 50 mm
O.D. pyrex tube. Each of these 4 tubes were joined to 6 mm
pyrex tubes by using O-ring joints. Figure 2.1 shows the
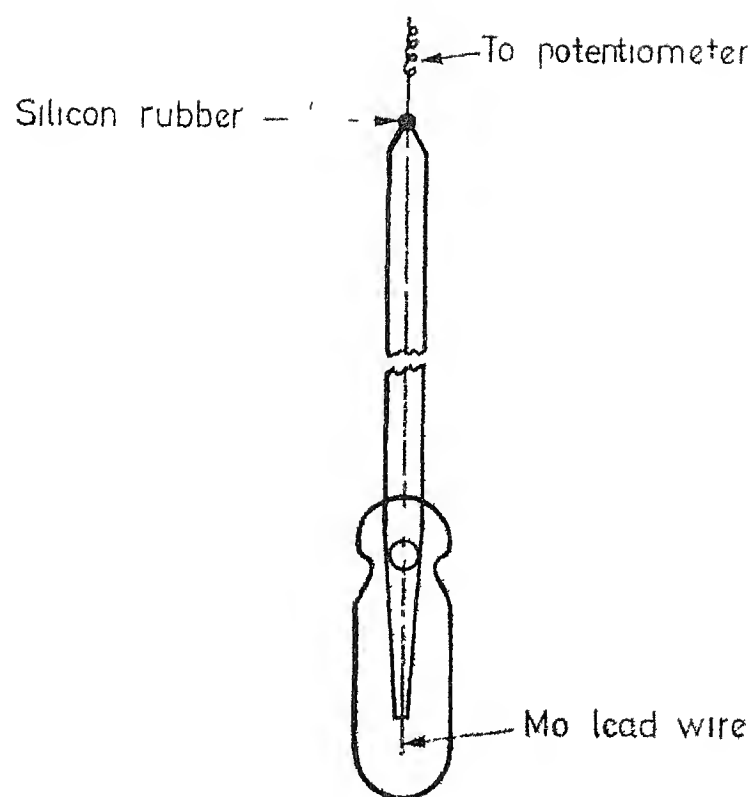details of the cell. The B-60 joint was prevented from

To potentiometer

Silicon rubber

Mo lead wire
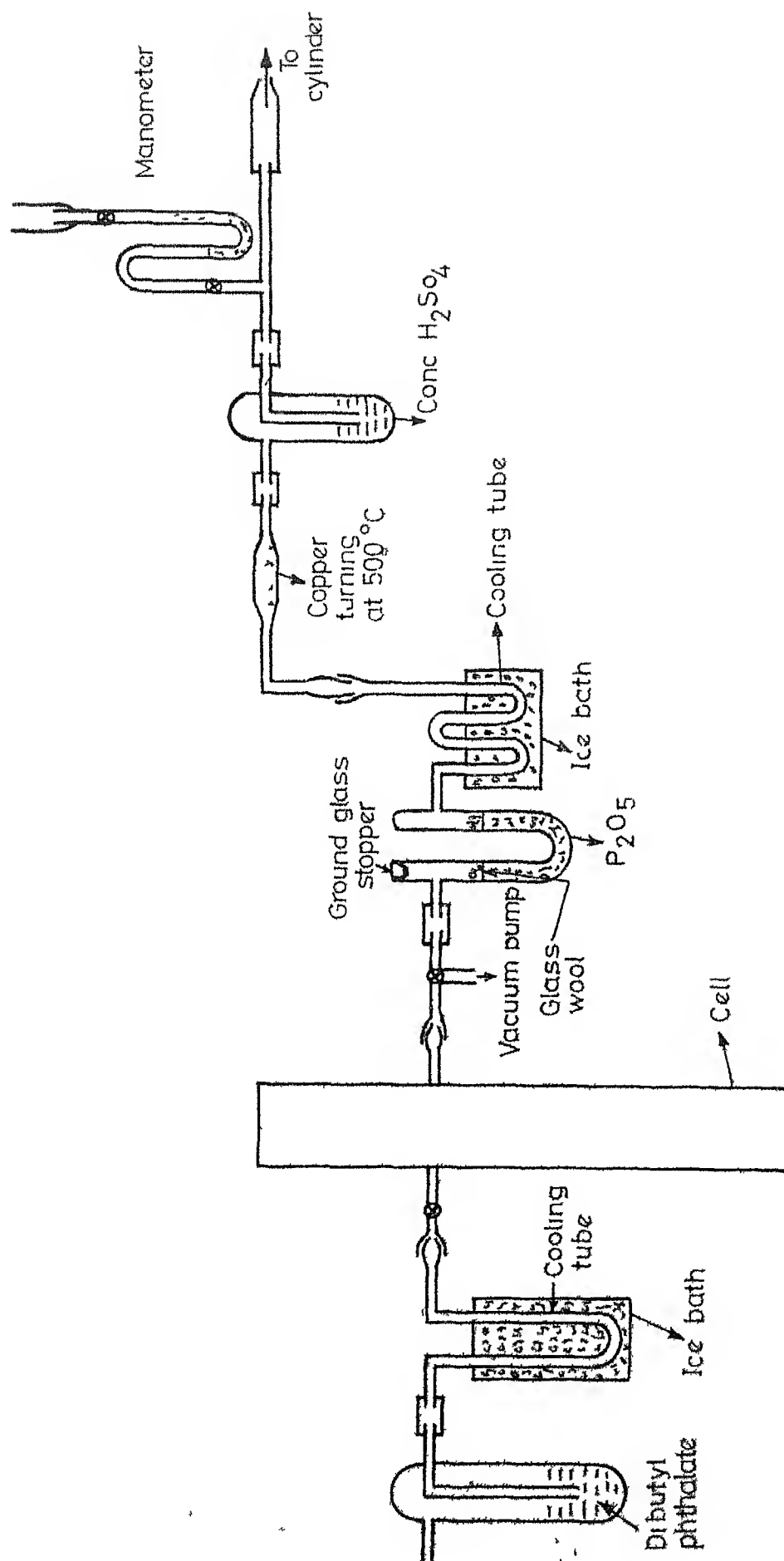
Fig. 3 2   The   Electrode

Fig. 3.3 Gas Purification Train

getting heated up by circulating water through a 6.5 mm diameter Cu tube wound around the joints.

The electrodes as shown in figure 3.2 were made of 6 mm O.D. Vycor tubes of 75 cms length. At one end of this tube was attached another Vycor tube of 2.5 mm diameter and 4 cms length. 1 mm diameter well annealed and cleaned molybdenum wires/were sealed inside these tubes. The wire projected about 3 mm at the tip of the 2.5 mm diameter tube. This tip was covered by a bulb of 6 cms length and 9.5 mm O.D. The bulb had 4 holes so that the alloys can be put inside and the electrolyte can get inside the bulb. The other end of the 6 mm Vycor tube was sealed under vacuum with silicon rubber.

3.3 Purification of Gas

The argon used was purified for oxygen and moisture by passing it through concentrated H_2SO_4, oxygen free copper turning heated to $500^{\circ}C$ and then passing it through P_2O_5. The details of the gas purification train is shown in figure 3.3. A U-tube manometer containing dibutyl phthalate was introduced into the system, so as to be able to fill the evacuated cell with argon properly. The gas coming out of the cell was cooled in a U-tube kept in a ice-bath and bubbled out in a bubbler containing dibutyl phthalate.

3.4 Vacuum System

The vacuum system used consists of a diffusion
pump backed by a rotary pump of model VS - 4 supplied by
Hindhivac Company. The assembly contains a liquid nitrogen
trap and a P_2O_5 trap to protect the oil from contamination

3.5 Temperature and E.M.F. Measuring Unit

A type K-4 potentiometer with a d.c. galvanometer
manufactured by Leeds and Northrup were used to measure the
e.m.f. of the cell. The potentiometer is capable of
measuring 0.5 microvolts in the range of 0.16 volts.

The 36 gauge chromel and alumel wires were first
annealed by passing a current at 40 volts. The homogeneity
of wires was tested by measuring the e.m.f. across a wire
when it is pulled through liquid nitrogen The length of the
wire showing constant e.m.f. was selected for making the
thermocouple. This wire was twisted and the bead was made
by striking arc with a mercury bath kept under kerosene at
40 volts. The hot junction of the thermocouple was passed
through a 6 mm diameter Vycor tube closed at the bottom.
The thermocouple tube was pushed inside the cell through
a 0-ring joint at the top of the cell. The cold junction
was made by soldering 18 gauge enamelled Cu-wires using a
$ZnCl_2$ flux and it was kept in a ice-water bath.

For measuring the e.m.f. of the cell the molybdenum lead wire were connected to 18 gauge enamelled Cu-wires by Cu-connectors. The copper and molybdenum lead wires were covered with polythene sleeves to protect them **from draught. These wires were fixed on stands** so as to protect them from moving and picking up stray e.m.f.

3.6 Experimental Procedure

3.6.1 Cleaning of the apparatus. The whole glass apparatus was first cleaned by chromic acid care was taken to avoid contact of chromic acid with the ground joints by applying ample amount of grease on the joints. The apparatus was then cleaned with alcohol followed by distilled water. Finally it was cleaned with demineralised water and assembled inside the furnace for drying at $120^\circ C$ for a period of 24 hours. After drying, the cell was flushed with argon for 2 hours to ensure complete removal of moisture.

3.6.2 Preparation of the electrolyte. The electrolyte was prepared using AR grade of $LiCl \cdot H_2O$, KCl and $PbCl_2$ of the following purity:

KCl

Free acid (as HCl) 0.0018

Free alkali (as KOH)
0.0028

Al   0.001

As   0.00004

Ba   0.001

Bromide and Iodide 0.005

Ca   0.001

Chlorate   0.003

Heavy metals (as Pb)
0.0005

Mg   0.0005

Phosphate   0.001

Na   0.02

Sulphate   0.001

Nitrogen   0.001

$LiCl \cdot H_2O$

Sulphate 0.04

As   0.0001

Fe   0.002

Pb   0.001

$PbCl_2$

Pure for analysis

Since the LiCl–KCl eutectic mixture cannot be effectively dehydrated by vacuum, the salts were dried separately by the following process. Appropriate amounts of $LiCl \cdot H_2O$, KCl and $PbCl_2$ were weighed to give approximately 104 cc of molten electrolyte. The volume of the molten electrolyte was determined by melting appropriate amounts of the salts in a separate 45 mm diameter pyrex crucible outside the cell. Three tubes of diameter 12 mm and 18 mm with optically flat bottoms and having holes at the other end

were placed inside the crucible. These tubes were filled with KCl and $PbCl_2$. LiCl was put in the crucible. Molybdenum wires were attached to the holes in the tubes containing KCl and $PbCl_2$. The crucible was lowered into the main quartz tube with the help of threads which passed through the holes in the crucible. The main cell was closed, all the O-ring joints were tightened and the vacuum pump was attached to the system.

When evacuation of the cell was started a lot of moisture started coming out. In order to protect the pumps the vacuum system was connected to the cell through a liquid nitrogen trap. The cell was evacuated at room temperature for 24 hours. It was then slowly heated to $40^{o}C$ and evacuated for 8 hours. The vacuum obtained in this much of time was only 50 microns because of slow process of moisture evolution. The cell was now attached to diffusion pump. With the help of a liquid nitrogen trap the cell was evacuated to 1.5×10^{-6} mm Hg. This vacuum was maintained for about 8 hours. To ensure complete removal of moisture the cell was slowly heated in steps of $5^{o}C$ to reach $120^{o}C$ in 6 hours while heating only the backing pump was used. At $120^{o}C$ the cell was evacuated to 1.5×10^{-6} mm of Hg and maintained for 6 hours. The temperature was increased slowly in steps of $5^{o}C$ to $150^{o}C$ in 7 hours. At $150^{o}C$ the cell was evacuated to 1.5×10^{-6}

mm of Hg for 12 hours to ensure complete removal of moisture. Now the temperature was raised to $500^\circ C$ at a rate of $25^\circ C$ per hour while the backing pump was operating. At $500^\circ C$ the cell was evacuated at 1.5×10^{-6} mm of Hg for 16 hours. Now argon was flushed at $500^\circ C$ for 15 minutes and the cell was evacuated immediately to 1.5×10^{-6} mm of Hg for 12 hours to remove any moisture carried by argon from rubber tube connections. Now argon was flushed and the temperature was lowered to $400^\circ C$. The joint was opened while a torch of argon was kept on the top of the cell. Now the tubes containing KCl and $PbCl_2$ were taken out with the help of Mo wires allowing the dry KCl and $PbCl_2$ powder to fall into the crucible containing LiCl. The cell was closed and evacuated. This operation took a few minutes. After evacuation for 2 hours at 1.5×10^{-6} mm of Hg argon was flushed for 15 minutes and the cell was again evacuated for an hour. Argon was introduced into the cell and the temperature was raised to $550^\circ C$. A positive pressure was maintained by the flow of argon. The electrolyte was now ready for experimentation

3.6.3 <u>Preparation of electrodes</u>   The lead and bismuth used for the preparation of alloys were 99.999 pct. pure. Appropriate amounts of lead and bismuth were weighed on an electronic balance to give 0.1, 0.3, 0.5, 0.7 and 0.9 mole fraction of lead in the alloy. The metals were sealed

under vacuum in a quartz tube and held 150°C above the liquidus temperature for 4 hours. The alloy was taken out by breaking the quartz tube and the process was repeated to ensure homogenisation of the alloy. The alloy was taken out and crushed to a powder of 1 mm particle size, and kept in a dessicator. The tips of molybdenum wires inside the bulbs of electrodes were cleaned by electrolysing in a concentrated NaOH solution[19] at 2 Volt d.c. at 3.5 Amps/cm² current density. The molybdenum-wire was the anode and a stainless steel wire was the cathode. The molybdenum tip was then washed with alcohol and dried.

3.6.4 Measurement of e.m.f.: When the electrodes and the electrolyte were ready the outlet stop cock of the cell was closed, the O-ring joints were made loose, the 6 mm blind tubes were taken out and the electrodes were inserted inside the cell chamber. They were kept over the crucible in the temperature range of 500°C. The O-ring joints were tightened and argon flow was stopped. The cell was evacuated for an hour. Argon was introduced into the cell and a positive pressure was maintained inside the cell. The electrodes were slowly rotated and pushed inside the crucible containing electrolyte. The molybdenum lead wires were connected to the potentiometer and the e.m.f readings were taken. It took about 8-12 hours. The temperature was then raised to 575°C and was brought back

$550^\circ C$. The e.m.f. was noted again as a function of time until it was constant. It took about a couple of hours. Now the temperature was lowered to $525^\circ C$ and was again brought back to $550^\circ C$. The e.m.f. was noted again until it was constant. ~~again~~. The values of the e.m.f. reported in Chapter - IV are the average e.m.f. values of the three e.m.f. readings. When the e.m.f. readings were taken the temperature of the cell was read simultaneously with the help of another potentiometer.

CHAPTER - IV

RESULTS

4.1 The Partial Molar Free Energy and the Activity of Lead

From the observed values of e.m.f. the partial molar free energies, $\Delta \bar{G}_{Pb}$, for the different mole fraction of lead i.e $X_{Pb} = 0.1 - 0.9$ can be obtained directly from the equation,

$$\Delta \bar{G}_{Pb,X_{Pb}} = - nFE$$

where

n = 2 (since the valence change occurring $Pb \rightarrow Pb^{++}$

   is 2)

F = Faraday constant 23061 cal/volt equivalent

E = The measured e.m.f. in volts

These $\Delta \bar{G}_{Pb}$ values are recorded in Table 4.1. The activities of Pb in liquid alloys can be obtained from the following equation,

$$\Delta \bar{G}_{Pb,X_{Pb}} = RT \ln a_{Pb} \tag{4.1}$$

These values of a_{Pb} are also listed in the same Table 4.1.

4.2 Partial Molar Free Energies of the Component in the Pb-Bi Alloys

With the help of excess partial molar properties we can proceed with the further calculations. These excess quantities are identified below by the superscript 'ex'. The excess partial molar free energies of lead can be calculated by the following equation,

$$\Delta \overline{G}^{ex}_{Pb,X_{Pb}} = \Delta \overline{G}_{Pb} - \Delta \overline{G}^{id}_{Pb} \qquad (4.2)$$

where

$$\Delta \overline{G}^{id}_{Pb} = RT \ln X_{Pb}$$

These excess free energies of formation of lead are calculated by taking $\Delta \overline{G}_{Pb}$ values from eq. 4.1.

The corresponding excess partial molar free energies of Bi are calculated by graphical integration of the Gibb's-Duhem eqn. of the following form[3]

$$\Delta \overline{G}^{ex}_{Bi,X_{Bi}} = - \alpha_{Pb} X_{Pb} X_{Bi} - \int_{X_{Bi}=1}^{X_{Bi}} \alpha_{Pb} \, dX_{Bi} \qquad (4.3)$$

where

$$\alpha_{Pb} = \frac{\Delta \overline{G}^{ex}_{Pb}}{(1 - X_{Pb})^2}$$

These α_{Pb} values calculated from the experimental data at X_{Pb} = 0.1, 0.3, 0.5, 0.7 and 0.9 were plotted as a function of composition. The values of α_{Pb} corresponding to data X_{Pb} = 0.2, 0.4, 0.6 and 0.8 were obtain from the same plot. From the areas obtained by Simpsons rule for each composition of Pb (i.e. X_{Pb} = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9) the $\Delta \bar{G}^{ex}_{Bi,X_{Bi}}$ values are calculated.

These partial molar quantities at $823^{\circ}K$ for the lead component and bismuth component in the liquid Pb-Bi alloys are listed in Tables 4.2 and 4.3 respectively.

$\bar{G}_{Pb}$ and $\Delta \bar{G}_{Bi}$ values for different composition are calculated from eq. (4.2). These values are also listed in Table 4.2 and 4.3. The activities of the components are calculated by eq. (4.1) and the corresponding activity coefficient, γ were calculated by formula $\gamma = a/X$. These activities and activity coefficients are listed in Tables 4.2 and 4.3.

The partial molar free energies are plotted in figure 4.1 and the partial molar excess free energies are plotted in figure 4.2. The activities and activity coefficients are plotted in figure 4.3. All the figures show expected and consistent behaviour of the alloys.

4.3 Integral Molar Properties

These values are obtained from the partial molar properties of lead and bismuth components by the following equations,

$$\Delta G = X_{Pb} \, \Delta \overline{G}_{Pb} + X_{Bi} \, \Delta \overline{G}_{Bi} \qquad (4.4)$$

and

$$\Delta G^{ex} = X_{Pb} \, \Delta \overline{G}^{ex}_{Pb} + X_{Bi} \, \Delta \overline{G}^{ex}_{Bi} \qquad (4.5)$$

The values of ΔG and ΔG^{ex} obtained for different compositions are listed in Table 4.4. These values are also plotted in figure 4.1 and 4.2 showing consistent behaviours.

The ΔH values calculated from the $\frac{dE}{dT}$ values obtained from data of e.m.f. measurements are not reliable[22,33,40]. Kleppa's[45] as reported values of ΔH at $623^{o}K$ and $723^{o}K$. His data shows that ΔC_p for these alloys is zero i.e. H is independent of temperature. Therefore his data at $723^{o}K$ are taken for further calculations. From this ΔH and our ΔG values, ΔS values are calculated and listed in Table 4.4. The ΔS and ΔS^{ex} values are plotted in figure 4.4 along with the values of ΔS^{id}. It may be noted that the S^{ex} values varies in a different way from the previous workers.

Table 4.1   E.m.f. obtained with the cell

$$Pb \; \left| LiCl + KCl + PbCl_2 \; (l \;) \right| \; (Pb+Bi)$$
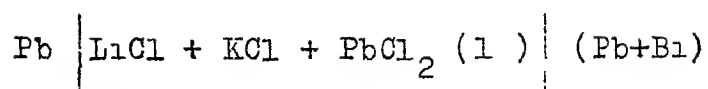
at $823^{\circ}K$

Composition of the alloy X_{Pb}	E.m.f. (Volts)	$\Delta \tilde{G}_{Pb}$ cal/mole	a_{Pb}
0.1	0.112,000 ± 0.00050	−5165	0.045
0.3	0.050,820 ± 0.00025	−2340	0.235
0.5	0.030,500 ± 0.00010	−1405	0.425
0.7	0.015,850 ± 0.000050	−730	0 640
0.9	0.003,550 ± 0.000003	−165	0.900

Table 4.2   Partial molar quantities for liquid Pb-Bi alloys at $823^{\circ}K$ (Pb component)

X_{Pb}	a_{Pb}	γ_{Pb}	$\Delta \bar{G}_{Pb}$ cal/mole	$\Delta \bar{G}_{Pb}^{x}$ cal/mole
0.0	0.000	(0.120)	$(-\infty)$	(-2320)
0.1	0.045	0.450	-5165	-1400
0.2	0.125	0.630	-3340	-710
0.3	0.235	0.780	-2340	-370
0.4	0.330	0.825	-1795	-295
0.5	0.425	0.850	-1405	-270
0.6	0.525	0.870	-1065	-230
0.7	0.640	0.915	-730	-145
0.8	0.775	0.970	-415	-50
0.9	0.900	1.000	-165	+7
1.0	1.000	1.000	0	0

Table 4.3   Partial molar quantities for liquid Pb-Bi
alloys at 823°K (Bi component)

X_{Bi}	a_{Bi}	γ_{Bi}	$\Delta \overline{G}_{Bi}^{ex}$ cal/mole	$\Delta \overline{G}_{Bi}$ cal/mole
1.0	1.000	1.00	0	0
0.9	0.875	0.97	−50	−220
0.8	0.725	0.91	−170	−535
0.7	0.600	0.86	−275	−855
0.6	0.500	0.84	−310	−1145
0.5	0.410	0.82	−330	−1465
0.4	0.315	0.79	380	−1880
0.3	0.215	0.72	−540	−2510
0.2	0.115	0.57	−930	−3560
0.1	0.050	0.50	−1155	−4920
0.0	0.000	(0.13)	− ∞	(−1170)

Table 4.4   Integral quantities for liquid Pb-Bi
alloys at 823°K

X_{Pb}	X_{Bi}	$\Delta H^{\oplus}$ cal/mole	ΔG cal/mole	ΔS cal/mole-deg	ΔG^{ex} cal/mole	ΔS^{ex} cal/mole-deg
0.1	0.9	-80	-715	0.772	-185	0.12
0.2	0.8	-155	-1095	1.142	-280	0.14
0.3	0.7	-210	-1300	1.324	-305	0.11
0.4	0.6	-245	-1400	1.403	-305	0.06
0.5	0.5	-250	-1435	1.440	-300	0.06
0.6	0.4	-235	-1390	1.403	-290	0.07
0.7	0.3	-205	-1265	1.288	-265	0.07
0.8	0.2	-150	-1045	1.088	-225	0.09
0.9	0.1	-80	-640	0.680	-110	0.03

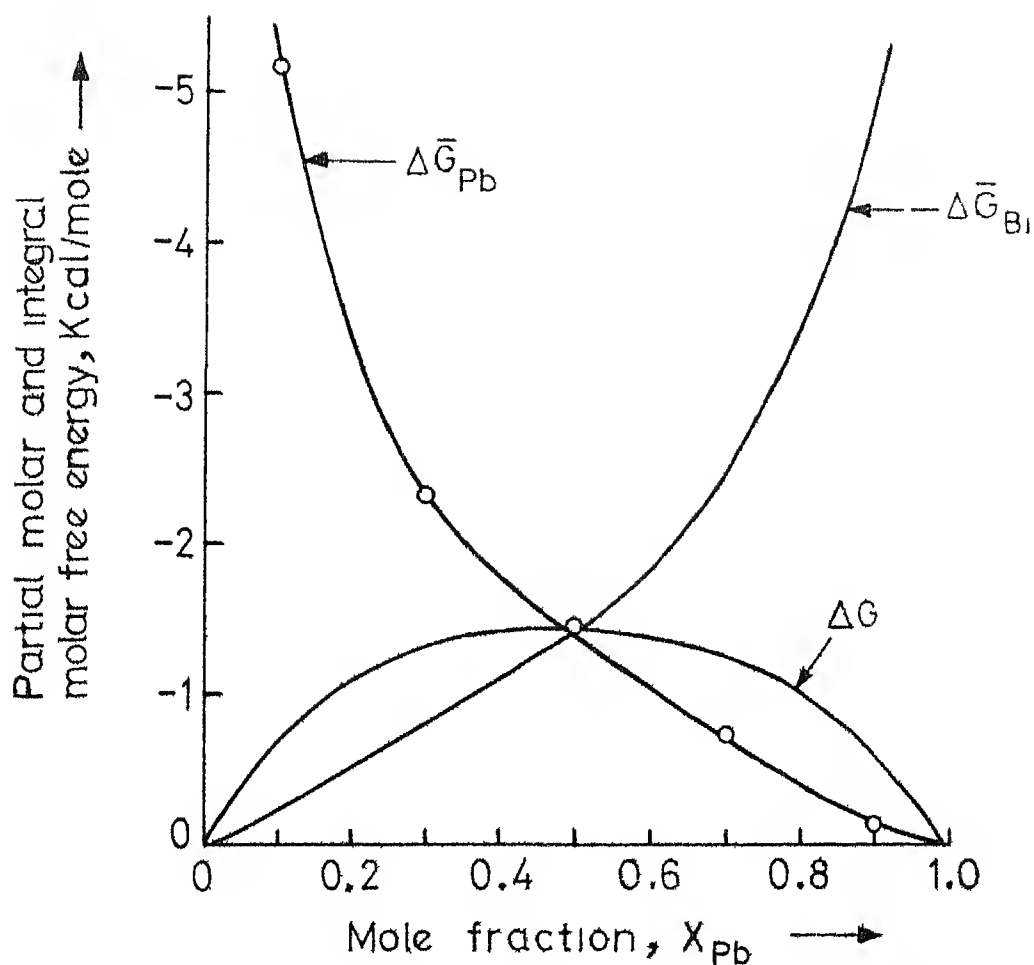$\oplus$ Values taken from reference (45).

Fig 4.1 Partial molar and integral molar free
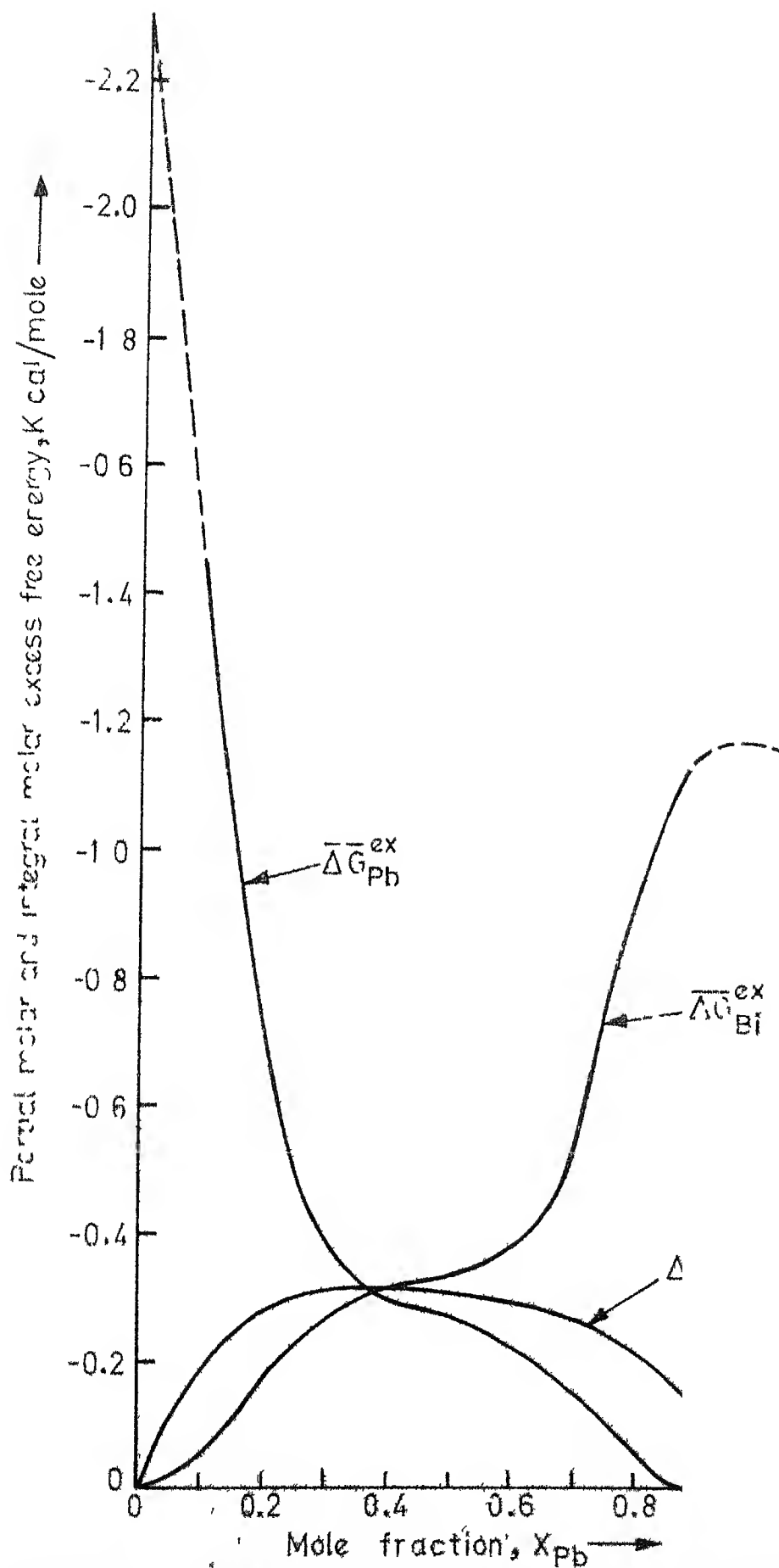erergies of the Pb-Bi alloys
at 823°K

Fig.4.2 The partial molar and integral molar excess free energies of the Pb-Bi alloys at 823°K
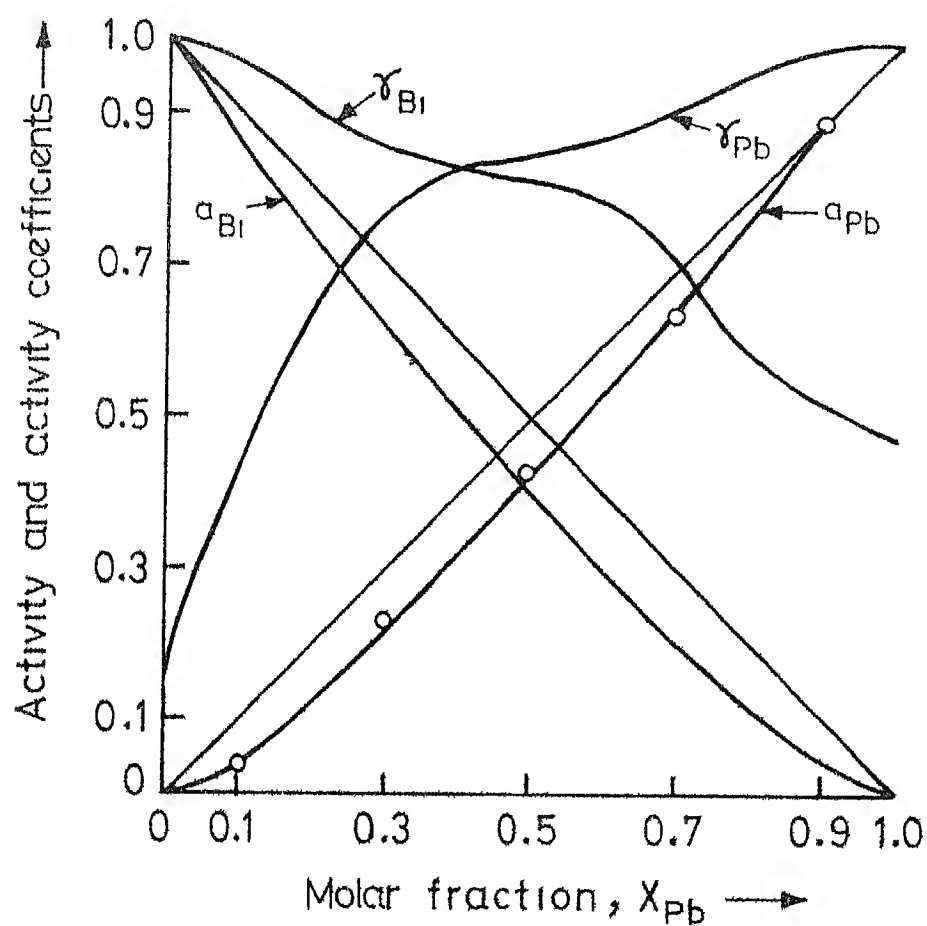
Fig.4.3 Activity and activity coefficients
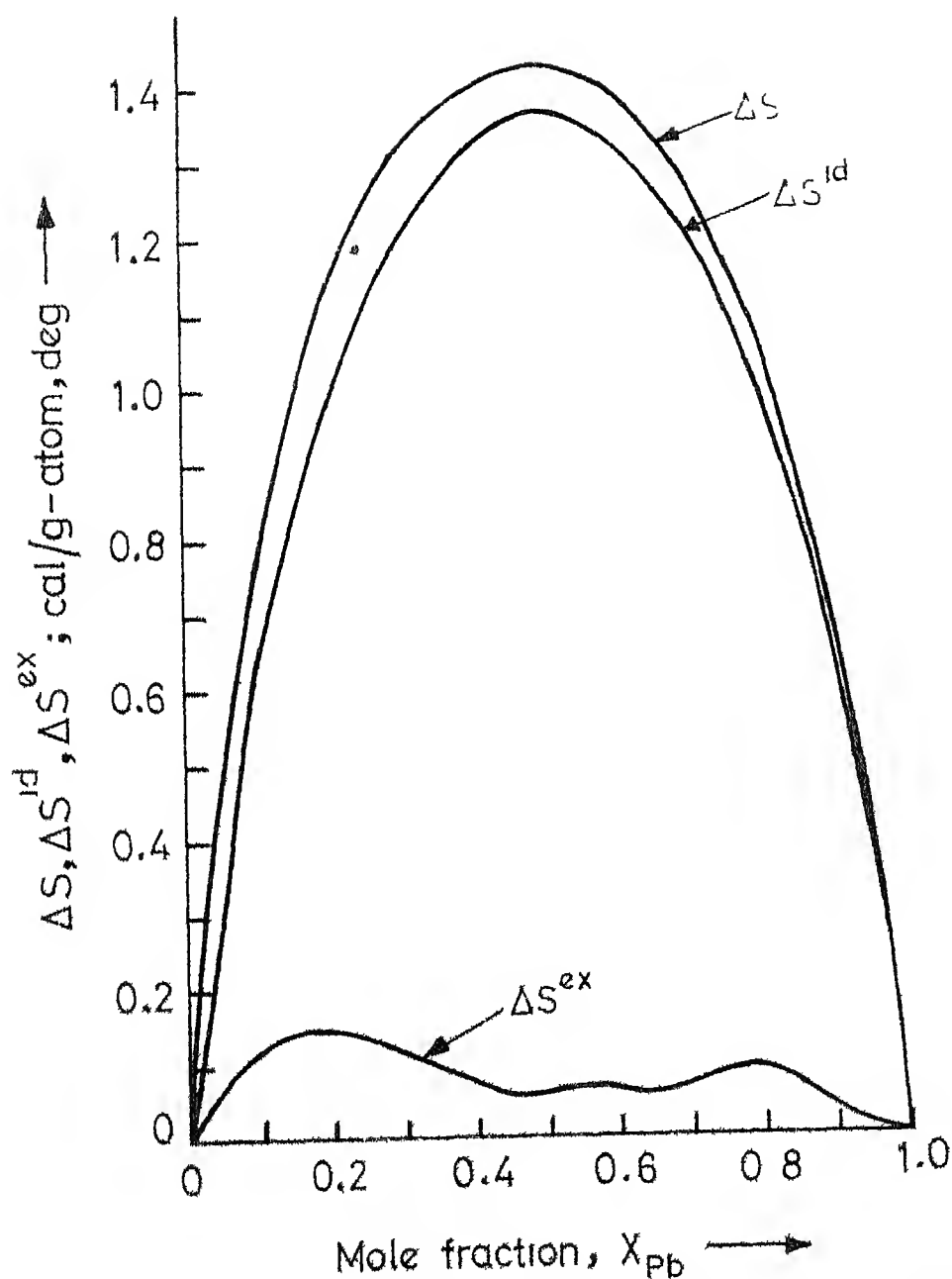of the components in the Pb-Bi
alloys at 823°K

Fig. 4.4 Entropy of formation, ideal entropy of formation and excess entropy of formation of Pb-Bi alloys at 823 °K.
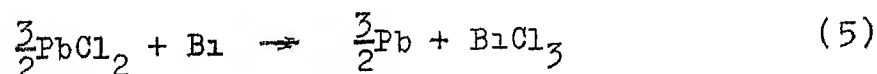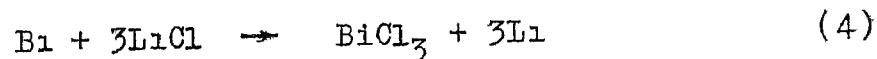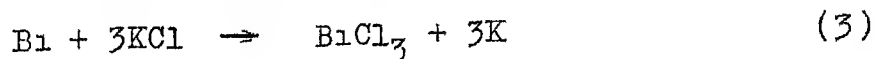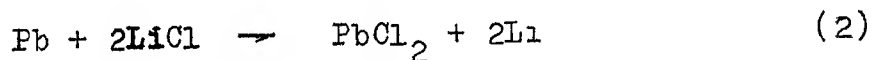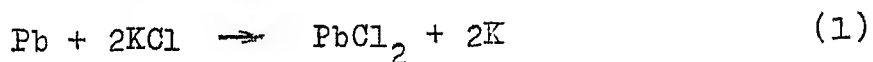
CHAPTER - V

DISCUSSIONS

5.1 Sources of Errors

The various sources of errors which can occur in the e.m.f. measurements are discussed below.

Side reactions   During the measurements secondary reactions i.e. reactions other than the cell reactions can give rise to errors. The following are the side reactions which may occur during the measurements

$$Pb + 2KCl \rightleftharpoons PbCl_2 + 2K \tag{1}$$

$$Pb + 2LiCl \rightarrow PbCl_2 + 2Li \tag{2}$$

$$Bi + 3KCl \rightarrow BiCl_3 + 3K \tag{3}$$

$$Bi + 3LiCl \rightarrow BiCl_3 + 3Li \tag{4}$$

$$\frac{3}{2}PbCl_2 + Bi \rightarrow \frac{3}{2}Pb + BiCl_3 \tag{5}$$

The activities of Li, K, and $BiCl_3$ are calculated on the basis of the standard free energies of formation of chlorides[2,3] and assuming equilibrium in all the above cases. Those values are tabulated below

Reaction	Activities
1	$a_K \simeq 10^{-27}$
2	$a_{Li} \simeq 10^{-23}$
3	$a_{BiCl_3} \simeq 10^{-71}$
4	$a_{Li} \simeq 10^{-70}$
5	$a_{BiCl_3} \simeq 10^{-14}$

These values are much smaller compared with the values calculated for the cells used in the literature   Therefore the side reactions are assumed to be negligible   From the activity of $BiCl_3$ it can be seen that the amount of bismuth going into the molten electrolyte is negligible. So the alloy electrode composition remains constant before and after the experiments.   Also the diffusion in liquid alloys is generally very high and the diffusion coefficient is of the order of 10^{-8} cm/sec.   So any small gradiation in the liquid electrode will tend to homogeneise rapidly.

The side reactions due to the impurities have been avoided   To avoid dust the whole system was thoroughly cleaned before use.   The molybdenum lead wires had an oxidised surface.   To remove it these were electrolysed to clean the surface   To make sure that the gas train does not introduce any impurities, the argon was purified and flushed through the gas tra n for 15 minutes, before

passing it through the main cell. To avoid side reactions due to moisture and volatile matter present in the electrolyte prolonged evacuation and heating as discussed in Chapter - III were carried out. Sufficient amount of $PbCl_2$ (1 mol. wt $\langle$) was added to avoid reduction of $PbCl_2$ by basor metals.

Stray e.m.f.: The stray e.m.f. produced by the furnace windings were reduced by chrome-plated earthed nickel sheet. The furnace was switched off for a second while the e.m.f. was being measured. This did not alter the cell e.m.f., confirming that there was no pick up of e.m.f. from the furnace windings. The contact potentials in the measuring units were reduced by using copper single strand wires. Any induced e.m.f. pick up by the measuring units were reduced by the copper earthed mesh over the copper lead wires. The contacts of the lead wires were kept clean and free from air circulation to avoid any e.m.f. pick up. Thus the stray e.m.f. which may alter the cell e.m.f. was avoided.

Reversibility of the cell   The reversibility of the cell was confirmed by the following manner. The furnace temperature was raised to a higher value and then the system was brought back to original temperature   The e.m.f. at this temperature was measured   Again disturbing

the system to lower temperatures and bringing it back to original temperature the e.m.f. was measured. Values of e.m.f. were found to be consistent at the temperature of measurement. The temperature was controlled to $\pm 1^{\circ}C$ during the measurements. On the basis of available partial molar enthalpies[48] it is found that at this temperature variation of $\pm 1^{\circ}C$ would have negligible effect on the e.m.f.

<u>Ionic conduction</u>. The cell must not have any electronic conduction. This arises at higher temperatures and from emulsion of metals in electrolyte and impurities. Precautions have been taken to minimise this Also the system itself has very low vapour pressure which will prevent evaporation of metals[46]. Evaporation generally leads to change of composition as well as electronic conduction.

5.2 Comparison With Other Data

The values of the $\Delta\bar{G}_{Pb}$ obtain in present work (Table 4.1) are consistent with the $\Delta\bar{G}_{Pb}$ values obtained by previous investigators[22,33,47]. The $\Delta\bar{G}_{Pb}$ values of lead reported by Strickler et al[22] and Elliott et al[33] are plotted in figure 5.1 along with those obtained by this study. This figure shows that both sets of data are close to the present results The data of

Elliott et al[33] at $773^{\circ}K$ are less negative than those reported in this investigation at $823^{\circ}K$. The results of Strickler et al[22] corresponding to $700^{\circ}K$ are also less negative. Thus the present results compare well with other data.

5 3 Internal Consistency of the Results

The internal consistency of the present results is confirmed by the following

1) From figure 4.1 it is observed that a_{Pb}, $-\bar{G}_{Pb}$, a_{Bi} and $\Delta\bar{G}_{Bi}$ show smooth regular behaviour with composition

2) The $\Delta\bar{G}_{Pb,X_{Pb}}$, $\Delta\bar{G}_{Bi,X_{Bi}}$ values obtained by the same cell at $848^{\circ}K$[49] were more negative than those obtained at $823^{\circ}K$.

3) The values of $\Delta\bar{G}_{Pb}$ at $823^{\circ}K$ calculated with the available ΔH[45] values and $\Delta\bar{G}_{Pb}$ at $848^{\circ}K$[49] were in good agreement with those obtained experimentally at $823^{\circ}K$.

5.4 The Bonding in the Pb-Bi Alloys

The entropy of formation ΔS is found to be more than the ideal entropy. This suggests that there are contributions other than the configurational entropy

which makes $\triangle S$ greater than $\triangle S^{id}$. These contributions
may be from vibrational entropy, as other contributions to
$\triangle S$ of the Pb-Bi alloy are expected to be negligible. This
excess entropy against composition curve shows two minimas
at $X_{Pb} = 0.45$ and $X_{Pb} = 0.65$. At these compositions the
positive contribution to $\triangle S$ appears to be less. This can
arise either because of clustering or seggregation. Around
the composition $X_{Pb} = 0.45$ the Pb-Bi phase diagram (fig.
5 2) shows a eutectic, which suggests that seggregation in
the liquid alloy at this composition may have been
present. The phase diagram also shows a compound at about
$X_{Pb} = 0.68$ This again suggests association in the liquid
state It is thus postulated that in the Pb-Bi alloys the
bonding is weaker which makes the $\triangle S$ more positive than
$\triangle S^{id}$ and also there is association in the liquid state
around $X_{Pb} = 0.65$ and seggregation in the liquid state
also around $X_{Pb} = 0.45$. This view is consistent with
the experimental $\triangle S^{ex}$ values and the phase diagram.

It may be noted that $\triangle S^{ex}$ values obtained from
the average free energy values[22,40] of the previous
workers and the calorimetric heats of formation of
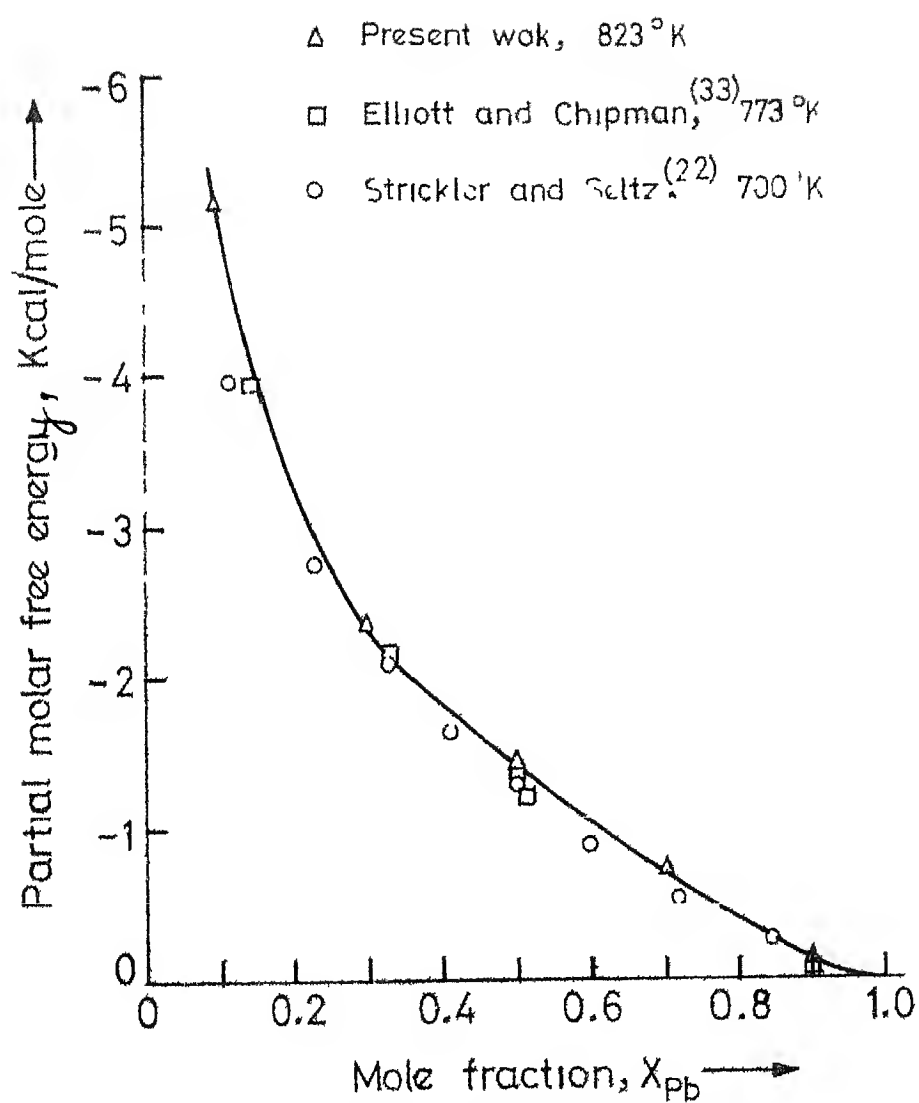Kleppa[45] do not seem to be consistent with the phase
diagram.

Fig. 5.1 Experimental values of the partial molar free energies of lead in the liquid Pb–Bi alloys
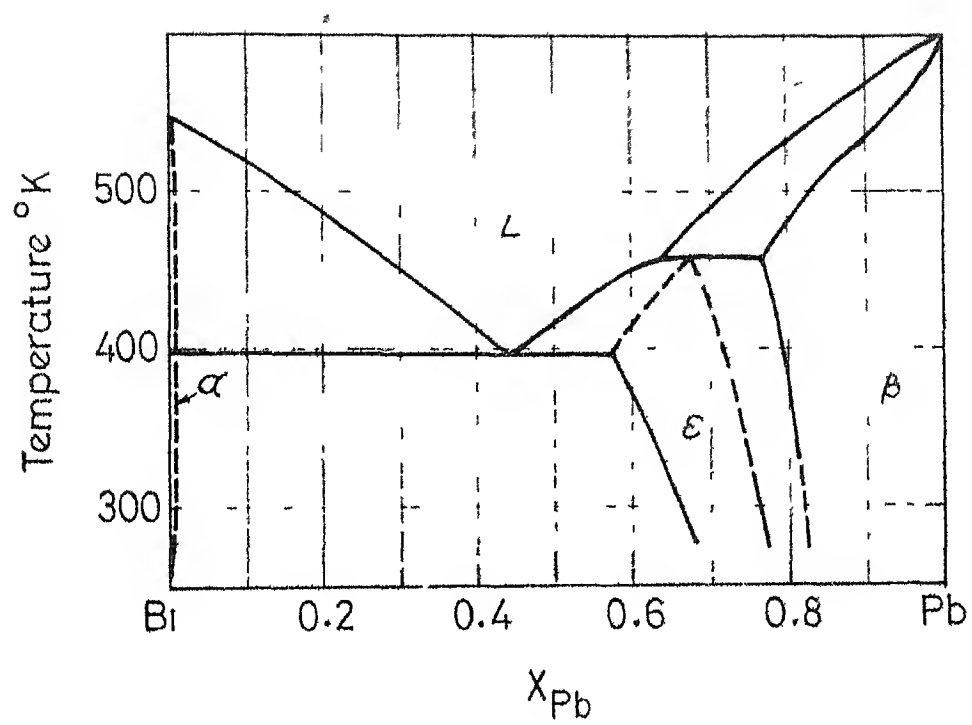
Fig. 5.2   Bismuth lead system

CHAPTER - VI

SUMMARY AND CONCLUSIONS

1. Activity of lead in lead-bismuth alloys $823^{\circ}K$ are measured at $X_{Pb} = 0.1, 0.3, 0.5, 0.7$ and 0.9 in the galvanic cell $Pb \mid LiCl + KCl + PbCl_2 \mid (Pb+Bi)$.

2. Activities and activity coefficients of lead and bismuth and $\Delta\bar{G}_{Pb}$, $\Delta\bar{G}_{Bi}$, $\Delta\bar{G}_{Pb}^{ex}$ and $\Delta\bar{G}_{Bi}^{ex}$ values at $823^{\circ}K$ are calculated, tabulated at $X_{Pb} = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1.0.

3. ΔG^{ex} and ΔG values for all compositions are tabulated.

4. By taking the calorimetric values[45] ΔS and ΔS^{ex} values are calculated.

5. All these thermodynamic functions are internally consistent, and consistent with other published data.

6. The variation of ΔS^{ex} with composition suggests that in the liquid alloy there is segregation at about $X_{Pb} = 0.45$ and association at about $X_{Pb} = 0.65$.

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